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THE ELECTROCHEMICAL OXIDATION
OF BARRIER-LAYER METALS

Introduction

As it is well known, the oxide films which possess rectified conductivity in electrolytes are the barrier-layer metals. They include aluminum, tantalum, niobium, zirconium and certain other metals [1]. Silicon and certain semi metals possess analogous properties [2]. Oxide films on aluminum have for a comparatively long time obtained wide application as dielectrics in electrolytic capacitors. Recently, a start has been made in using tantalum and niobium for these purposes. Many attempts at the practical use of the barrier-layer properties of oxide films on aluminum and tantalum in electrolytic rectifiers were made in the early thirties [3]. Now there is renewed interest in this question [4]. The application of oxide films in dry capacitors also possesses significant interest [5], cryotrons [6], relays [7], and so forth. Oxide films on semiconductor materials allow the obtaining of good protection of the surface of semiconductor instruments from external influences [8, 9].

In all cases of application, the oxide films on barrier-layer metals and semiconductors are obtained by electrochemical oxidation (formation) in electrolytes, without dissolving the metal and its oxide. Water solutions of different acids, and also pure salt-free water are used as such electrolytes [9, 10].

In spite of the numerous attempts to give an analysis of mechanism of formation of oxide films during electrochemical oxidation of barrier-layer metals, this question is not yet fully clear. To date, we do not have available the exhaustive data, which would allow

clarification of the role of the electrical field and the nature of the particles which diffuse through the oxide layer in the process of its growth. In exactly the same way we do not have experimental data, which would allow the complete explanation of processes, taking place on the boundaries metal -- oxide and oxide -- electrolyte.

Apparently it is possible to assume that if the metal is in contact with its own oxide, solution of the metal in the oxide takes place via the reaction



Metallic ions pass into the interstices of the oxide lattice and diffuse through the oxide layer to its boundary with electrolyte, where they react with hydroxyl ions forming a new oxide layer. Since the oxygen ion is significantly larger than the ions of the barrier-layer metals, introduction of excess of anionic component in the interstices of the oxide lattice is quite unlikely [11].

The problem of the mechanism of diffusion of metallic ions in the oxide lattice is also not clear at the present time. Usually, it is considered that the metallic ions diffuse through the interstices, however experiments with radioactive tantalum [12] showed that diffusion through vacancies is also possible, the more so, because according to Verwey [13], the oxide layer on aluminum contains a large number of cation vacancies, whereas all oxygen sites are filled.

Processes taking place on the oxide -- electrolyte boundary are studied in less detail than processes taking place in the system metal--oxide. Early theories, which considered the process of formation of the oxide layer as a purely chemical process, are rejected today, since they are not confirmed by experiment. A survey of these theories is given in the works [14, 15]. In reference [16] an attempt was made to consider the oxidation as an electrochemical process on oxide--electrolyte boundary. In this case, diffusion of hydroxyl ions through the double layer and the interaction of these ions with the metal in oxide lattice are assumed. Without going into a detailed analysis of this theory, we shall only indicate that it does not allow us to make any quantitative calculations whatsoever, since we do not know the activation energy for discharge of hydroxyl ions and the magnitude of the change in electrode potential of the metal. Kronsbein [17] has shown that, in considering processes taking place on the oxide -- electrolyte boundary, one should consider solution of the oxide in the electrolyte during the formation process.

PROCESSES TAKING PLACE IN THE OXIDE LAYER AND ON THE METAL--OXIDE BOUNDARY

1. Potential barrier on the metal--oxide boundary.

Let us assume that the growth of the oxide film occurs as a result of diffusion of metallic ions traveling from the metal to the vacancy in the oxide lattice. In order to pass through the metal--oxide boundary, the metallic ion must surmount the potential barrier which is located a distance a from the initial position of the ion in the metal (Fig. 1) [18]. The height of this barrier W_1 will be determined by thermal effect of the reaction (1) and the activation energy for motion of metallic ion into the interstitial region [19]. Gulbansen and Wysong [20] found a value of the order of 1 ev for the barrier height W for oxidation of aluminum in oxygen at a temperature 350--450°.

During electrochemical oxidation, the presence of an electric field E lowers the barrier by the magnitude qaE (q --charge of ion). Cabrerra and Mott [21] assume that the ion, upon passing the potential barrier at the metal--oxide boundary, can freely diffuse through the oxide layer via the interstices. In this case, growth rate of the oxide layer will be determined by the equation

$$\frac{dx}{dt} = N_s v_s \Omega \exp\left(-\frac{W_1 - qaE}{kT}\right), \quad (2)$$

where x --thickness of the oxide layer formed during the time t ; N_s --number of metallic ions "prepared" for transition through metal-oxide boundary per unit of surface of this boundary; v_s --frequency of oscillation of the ions; Ω --volume of oxide per ion of metal.

From (2) it follows that ion current density through oxide layer will be

$$j = qN_s v_s \exp\left(-\frac{W_1 - qaE}{kT}\right). \quad (3)$$

Gyuntershul'tse and Bets [1], investigating the anode oxidation of aluminum, obtained the experimental dependence for the ion current

$$j = j_0 \exp(\beta E). \quad (4)$$

From their values of $\gamma = 3.6 \times 10^{-23} \text{ a/cm}^2$ and $\beta = 4.25 \times 10^{-6} \text{ cm/v}$, Charlesby [22] obtained other values for aluminum: $\gamma = 10^{-18} \text{ a/cm}^2$ and $\beta = 3 \times 10^{-6} \text{ cm/v}$.

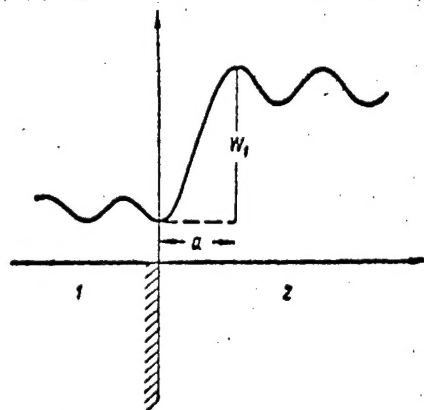


Fig. 1. Potential barrier at the metal-oxide boundary by Mott and Gurney [18].

1--metal ; 2--oxide.

If one were to take for aluminum, according to [18], $N_s = 10^{15} \text{ cm}^{-2}$, $q = 3e$, $\nu_s = 10^{12} \text{ sec}^{-1}$ and $kT = 0.025 \text{ ev}$, then for γ and β , we get from Gyuntershul'tse and Bets: $\underline{a} = 3.5 \times 10^{-8} \text{ cm}$ and $W_1 = 1.8 \text{ ev}$, and for the values of Charlesby, $\underline{a} = 2.5 \times 10^{-8} \text{ cm}$ and $W = 1.52 \text{ ev}$.

The values found for the barrier height W_1 differ materially from the values obtained by Gulbransen and Wysong.

Since the values of N_s and W_1 in equation (2) pertain to the metal--oxide boundary, the growth rate of the oxide layer should be anisotropic. Actually, according to [23], the chemical oxidation rates in oxygen for various grain sizes of the single aluminum crystal vary by more than 30%. However, it was established in work [24] that the anode oxidation rates of aluminum on the (100) and (110) faces are virtually identical. Dewald [2], investigating anode oxidation of single crystals of InSb, arrived at the same conclusion.

It follows from Eq. (2) that the anode oxidation rate should

depend on temperature. However, in Eq. (4) of Gyuntershultse Bets and Charlesby, the coefficient β does not depend on temperature. In references [25, 26] it is shown convincingly that the anode oxidation rate of tantalum does not depend on the temperature in the interval $0 - 80^\circ$. The same result was obtained for temperature range -63 to $+90^\circ$ [27].

All the enumerated contradictions of experimental data and theory lead us to think that Cabrerra and Mott made an unfounded assumption on free motion of metallic ions through the interstices of the lattice. It is quite obvious that this ion should possess a definite activation energy in the transition of the metallic ion from one interstitial position to a neighboring one [28].

2. Electric field in the oxide layer.

It is natural to assume that the oxidation rate can be determined not only by the speed of transition of the ion through the metal--oxide boundary, but also by the diffusion rate of the ion through the interstices of the oxide lattice. In the presence of an electrical field, the transition probability of the ion from the metal to the oxide will, as before, be determined by the factor

$$v_1 \exp\left(-\frac{W_1 - qaE}{kT}\right), \quad (5)$$

while the transition probability of the ion from one interstice to the next by the factor

$$v_2 \exp\left(-\frac{W_2 - qbE}{kT}\right), \quad (6)$$

where W_2 -- activation energy for this transition, b -- half the distance involved in this transition and ν -- frequency of oscillations of the metallic ion in the interstices of the oxide lattice.

If the rate of the second process is much larger than the first, the oxidation rate will be controlled only by potential barrier at the metal--oxide boundary and the process will be described by equation (2). If, however, the speed of transition of the metallic ions in the oxide will be larger than the speed of their diffusion through the oxide layer, then a volume positive charge will be formed near the metal--oxide boundary distorting the field, that is effective in the oxide layer. The change of the field on the metal--oxide boundary will occur as long as the speed of transition of the metallic ions through this boundary will

not become equal to their diffusion rate through the oxide layer.

According to [29], the ion current, which determined by the ionic diffusion through the oxide layer, will be

$$j = 2qbnv \exp\left(-\frac{W - qbE}{kT}\right). \quad (7)$$

The current which is determined by the transition of ions through the metal--oxide boundary will, as before, be determined by equation (3).

After establishment of equilibrium, the number of ions entering into the oxide will be equal to number of ions passing through the oxide to its boundary with the electrolyte. Under this condition, the currents, determined by equations (7) and (3), will be equal. Hence one can determine the equilibrium number of ions n_0 passing through the metal--oxide boundary and reaching the oxide--electrolyte boundary, if it is assumed that for $x = 0$ the field is identical in both equations, and is equal to E_0 :

$$n_0 = \frac{(qN_s v_s)^{\frac{1}{a}}}{2qbv} \cdot j^{\left(1 - \frac{1}{a}\right)} \exp\left(\frac{W_2 - \frac{b}{a} W_1}{kT}\right). \quad (8)$$

The field E_0 which acts at the metal--oxide boundary during establishment of the process can be determined from equation (3) or (7):

$$\left. \begin{aligned} E_0 &= \frac{kT}{qa} \ln \frac{j}{qN_s v_s} + \frac{kT}{qa} \cdot \frac{W_1}{kT}; \\ E_0 &= \frac{kT}{qb} \ln \frac{j}{2qbn_0 v} + \frac{kT}{qb} \cdot \frac{W_2}{kT}. \end{aligned} \right\} \quad (9)$$

For calculation of field, acting in oxide layer, one can use Poisson equation

$$\frac{\partial E}{\partial x} = \frac{4\pi nq}{\epsilon}, \quad (10)$$

where n --concentration of ions in the oxide layer at a distance x from the metal--oxide boundary and ϵ --dielectric constant of the oxide.

From the condition of continuity of the ion current and equations (7), (9) and (10), we get

$$E(x) = E_0 + \frac{kT}{qb} \ln \left(1 + \frac{qb}{kT} \cdot \frac{4\pi n_0 q}{\epsilon} x \right). \quad (11)$$

The resultant equation shows the change in the field with thickness of the oxide layer. Only the mean value of field, acting in the oxide layer, can be determined in the formation process (ratio of the voltage applied to the formation cell to the thickness of the oxide

layer: $E_{av} = \frac{U}{\delta}$. From (11), by averaging over x for values from $x = 0$ to $x = \delta$, we find:

$$c_p = \alpha V$$

$$E_{cp} = E_0 + \left(\frac{kT}{qb} \right)^2 \cdot \frac{\epsilon}{4\pi n_0 q \delta} \cdot \left\{ \left(1 + \frac{qb}{kT} \cdot \frac{4\pi n_0 q}{\epsilon} \delta \right) \times \right. \\ \left. \times \left[\ln \left(1 + \frac{qb}{kT} \cdot \frac{4\pi n_0 q}{\epsilon} \cdot \delta \right) - 1 \right] - 1 \right\}. \quad (12)$$

It follows that from equation (12) the field strength during formation should change with the thickness of oxide layer. In reality, it is well-known [30] that when the formation is carried out at constant current density, then the field E_{av} does not depend on the thickness of the oxide layer and remains constant during the entire time of formation.

3. Influence of space charge of cation vacancies.

For explanation of the non-correspondence between equation (12) and experiment, the assumption was made by Young [31] that it is necessary to consider not only the entering of cations into the oxide layer from the metal, but also the formation in this layer of Frenkel defects under the action of a strong electric field. If one were to assume that ions, passing over from the lattice sites to the interstices, are carried by field, then it is necessary to consider that a negative space charge of cation vacancies appears in the oxide layer. This charge can in significant measure compensate the positive space charge of metallic ions near the metal--oxide boundary.

The Poisson equation for the case under consideration will have the form:

$$\frac{\partial E}{\partial x} = \frac{4\pi q}{\epsilon} (n - p), \quad (13)$$

where n , as before, is the concentration of metallic ions in the space charge region, and p is the concentration of cation vacancies which is constant over the thickness of oxide layer.

From the condition of continuity of the ion current we obtain, by differentiating equation (7):

$$\frac{\partial n}{\partial x} + n \frac{qb}{kT} \cdot \frac{\partial E}{\partial x} = 0. \quad (14)$$

Hence one can determine the cation concentration n , and then integrate equation (13) to find the expression for field strength E , that is effective in the oxide layer

$$E(x) = E_0 + \frac{kT}{qb} \ln \left[\frac{n_0}{p} - \frac{n_0 - p}{p} \exp \left(- \frac{qb}{kT} \cdot \frac{4\pi n_0 q}{\epsilon} x \right) \right]. \quad (15)$$

In this equation, E and n_0 have the same meaning as above.

The exponential factor in (15) decreases very rapidly with increase in x ; therefore, we get for the mean value of the field at $x = \delta$:

$$E_{cp} = E_0 + \frac{kT}{qb} \ln \frac{n_0}{p}. \quad (16)$$

and after substitution of E_0 from (9),

$$E_{cp} = \frac{kT}{qb} \left(\ln \frac{j}{2qbvp} + \frac{W_2}{kT} \right). \quad (17)$$

The resultant expression shows that the mean value of the field which is effective in the oxide layer during formation, does not depend on the thickness of this layer. This result agrees well with experiment.

In the electrochemical oxidation of barrier-layer metals a linear dependence of the voltage on the oxide layer and the thickness of this layer from the time of formation is observed if the current density remains constant. Such a dependence, taken for the electrochemical oxidation of aluminum in a water solution of boric acid (30 g/l) and borax (0.05 g/l) at a current density of 5 ma/cm², is shown in Fig. 2.

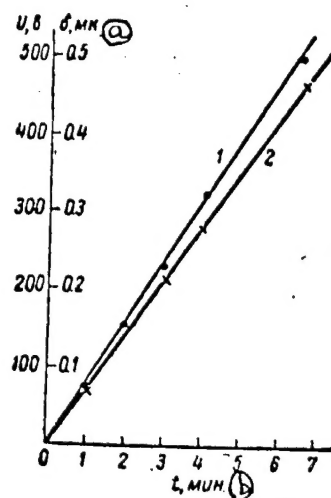


Fig. 2. Dependence of the voltage on the oxide layer and the thickness of the layer from time of formation.

1-- voltage; 2-- thickness.

a) U , volts; δ , microns. b) t , min.

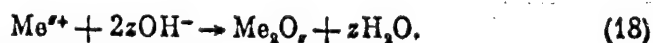
From these graphs, it is clear that in the formation process, the electrical field applied to oxide layer, the intensity of which is equal to $\frac{U}{\delta}$, remains constant during the entire time of formation.

The problem of formation of a space charge in anode oxidation is of great interest in explaining the mechanism of electrolytic rectification. A number of authors [32, 33], in explaining the mechanism of such rectification, have started out from assumptions on the existence of space charge in the oxide layer. We do not have direct proofs for the existence of such a charge. Moreover, Vermilyea [34], on the basis of measurements of the capacitance of oxide films on tantalum, arrived at the conclusion that if a space charge exists on the film, then it is minute and cannot play an essential role in electrical processes, occurring in the oxide film.

ELECTROCHEMICAL PROCESSES TAKING PLACE ON THE OXIDE--ELECTROLYTE BOUNDARY

In the investigation of the mechanism of anode oxidation of barrier-layer metals, it is not possible to limit the discussion only to consideration of processes taking place on the metal--oxide boundary and in oxide layer. In order that the oxidation reaction take place, it is necessary for the ions to approach the surface of the oxide layer. Under certain conditions, this process can be the controlling one.

The final stage of the electrochemical process will be a reaction on the surface of the oxide layer:



Besides this reaction, the discharge of hydroxyl ions with isolation of gaseous oxygen or with absorption of oxygen on the oxide layer is also possible. Tomashov [35] showed that the process of formation on the anode of an oxide layer is thermodynamically more probable than absorption and oxygen evolution, and will occur at less positive potentials ($\varphi_{\text{eq}}^{\text{Me}_2\text{O}} < \varphi_{\text{eq}}^{\text{O}_2}$):

$$\varphi = \varphi_0 + 0.826 - 0.059 \text{ pH}. \quad (19)$$

From this expression it is clear that the equilibrium potential for oxide formation depends on the pH of the solution and through the intermediate φ_0 on the individual properties of the metal and its oxide [36].

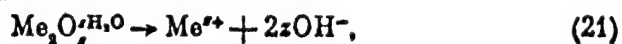
The rate of discharge of OH^- ions at the anode will be determined by the activation energy W_0 of the reaction (18). In the transition through the double layer the ionic free energy decreases by the value $\alpha e \varphi$, where $\varphi = \varphi_{\text{eq}}^{\text{Me}_2\text{O}} + \Delta \varphi$ and α is the proportionality factor. The shift of the electrode potential from equilibrium depends on the external field E that exists in the electrolytic cell. The plate current, which is determined by the discharge rate of OH^- , will depend on the values of W_0 and $\Delta \varphi$:

$$j = k \exp\left(\frac{W_0 - \alpha e \Delta \varphi}{kT}\right). \quad (20)$$

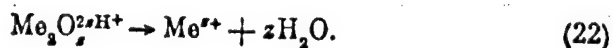
Equation (20) cannot be used for calculation of the rate of formation of the oxide layer, since the shift of potential changes continuously in the process of growth of the oxide layer, and cannot be given analytically. Attempts to avoid this difficulty [16] have not given positive results to date.

The analysis of processes, occurring during anode oxidation on the oxide--electrolyte boundary, forces one to give up representations on the continuity of the oxide layer.

It is quite obvious that independently of the choice of electrolyte some solution should occur in its oxide layer. If electrolyte is neutral, then reaction of chemical solution will have the form



and for acid electrolyte



The process of solution will take place simultaneously with formation of the oxide layer. At every given moment of time, the thickness of oxide layer formed is proportional to the voltage on the terminals of the electrolytic cell $x = aU$. Here solution of the thicker sections of the layer will occur on the surface of the layer; the process of formation of the oxide is delayed on these sections. At the same time, on other sections, whose thickness is still insufficient so that the ion current through them has ceased, formation of new layers of oxide will take place.

While the current density of formation is kept constant, the reaction of oxide layer formation predominates over solution reaction and thickening of the oxide layer takes place. If one were to stop the increase in voltage, then the oxide layer will form, its growth rate will start to be reduced and the ion current will drop. At some time, reaction rate of oxide formation and its solution will become identical and a certain residual ion current will be established. It is also necessary to consider that a current will be added to this current; this new current flows through the defects to the film at places of alien inclusions on the surface of metal. For a given value of voltage, temperature and pH of the electrolyte dynamic equilibrium will exist between the oxide layer and the electrolyte. Any change of these conditions will

shift the equilibrium to one side or the other, and change the magnitude of the residual current. Such representations of the interaction of the oxide layer with the electrolyte and of the nature of the residual current agree well with the well-known regularities of electrochemical oxidation of barrier-layer metals [1, 30].

The dissolving action of the electrolyte is connected with the so-called "effectiveness of current" during anode oxidation [17]. If one were to assume that Faraday's law is observed during anode oxidation of barrier-layer metals, then the thickness of the oxide layer for a constant density of the formation current will depend linearly on the time of formation

$$\delta = kjt. \quad (23)$$

$$k = \frac{a}{D} \alpha,$$

where a is the ratio of molecular weights of the oxide and the metal, D is the density of the oxide in the film and α is the electrochemical equivalent of oxygen.

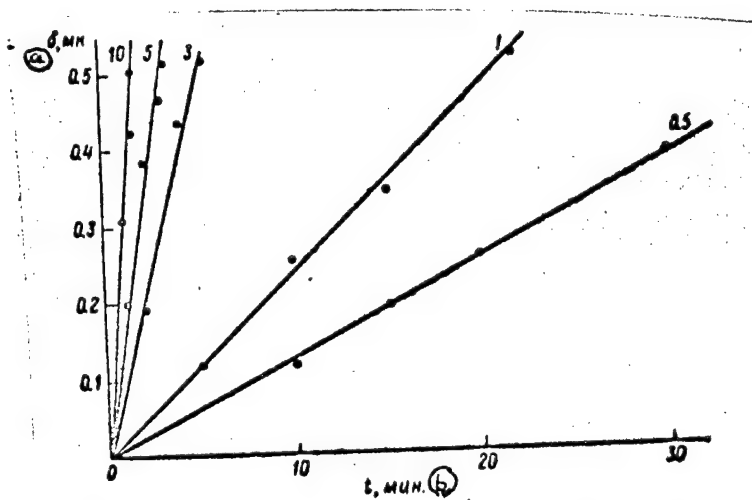


Fig. 3. Dependence of the thickness of the oxide layer on the time of formation for current densities from 0.5 to 10 ma/cm².

a) m̄crons; b) t, min.

Considering the solution rate of the oxide layer as the rate of heterogeneous chemical reaction at the boundary of the solid and liquid phases, one can determine decrease in thickness of the oxide layer as a result of solution:

$$\Delta\delta = C \exp\left(-\frac{W}{kT}\right) \Delta t. \quad (24)$$

Here W is the activation energy of the reaction of solution and C is the constant of this reaction.

From (23) and (24) we find the expression for the rate of formation of the oxide layer:

$$\frac{d\delta}{dt} = kj - C \exp\left(-\frac{W}{kT}\right). \quad (25)$$

Hence it is easy to see that with increase in the density of the formation current, the rate of growth of the oxide layer will increase as a result of the decrease of the role of the second term in the equation. However, for large current densities, heating up of the oxide surface will increase the rate of solution and the rate of growth should decrease.

We performed an investigation of the rate of growth of the oxide layer during anode oxidation of aluminum in a water solution of boric acid (30 g/l) and borax (0.05 g/l) at temperatures 40 to 80° for different values of the formation current density. The thickness of the oxide layer was determined by capacity measurements at a frequency of 1 kilocycle.

For all values of the current density a linear dependence of the thickness of the layer on the time of formation was obtained (Fig. 3). From the data of Fig. 3, the growth rate of the oxide layer was determined. The results obtained (Fig. 4) fit well the presentation given above on the influence of chemical solution on the rate of formation of the oxide layer. As follows from equation (25), the rate of growth of the oxide layer increases with growth in the density of the formation current. For high current density, when the heating of the oxide layer becomes significant, the rate of growth decreases. Increase in the electrolyte temperature decreases the growth rate of the layer as a result of increase in the solution.

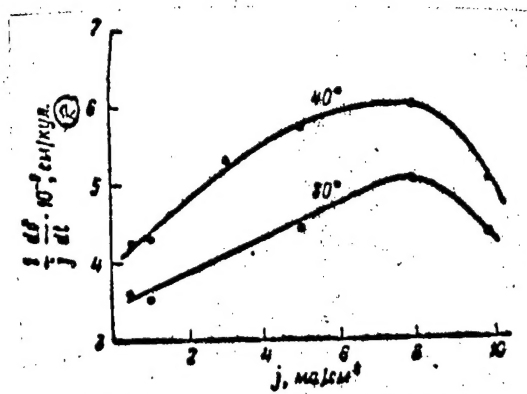


Fig. 4. Dependence of the growth rate of the oxide layer on the current density.

a) cm/coul.

CONCLUSION

The mechanism of formation of the oxide layer during electrochemical oxidation of the barrier-layer metals is extraordinarily complicated. As can be seen from the analysis of possible processes taking place on the metal--oxide boundary, in the oxide layer, and on the oxide--electrolyte boundary, any of these processes may be controlling. Apparently, for a comprehensive description of the mechanism of electrochemical oxidation, it is necessary to consider the action of all these processes simultaneously. It is especially necessary to emphasize the essential role of the complex structure of the oxide layer. Probably, it will be impossible to construct a rigorous theory of the electrochemical oxidation of the barrier-layer metals, if one were to be rejected the representations of the oxide film in the electrolyte as a complicated micro-galvanic system [37, 38]. In this connection, let us note that the representation of the mechanism of chemical oxidation of metals in oxygen developed by Cabrera and Mott [21] must be very carefully applied in the case of electrochemical oxidation, as certain authors do [25, 28, 29].

LITERATURE

1. A. Gyuntershul'tse and G. Bets. Electrolytic capacitors. Oborongiz, M. --L., 1938.
2. J. F. Dewald, J. Electrochem. Soc., 104, 4, 244, 1957.
3. A. Gyuntershul'tse. Electrical rectifiers and barriers. GEI, M, 1932.
4. K. Lehoeck. Rectifying device. Patent of the United States, 317233, No. 287739.
5. H. H. Remish, Elektro-Technik, 41, 46, 406, 1959.
6. S. M. Meade, Proc. IRE, 48, 46, 359, 1960.
7. K. O. Otley. R. F. Shoemaker, P. J. Franklin, Proc. IRE, 46, 10, 1723, 1958.
8. M. M. Atalla, E. Tannenbaum, P. J. Franklin, Bell Syst. Tech. J., 38, 3, 749, 1959.
9. L. L. Odynets, V. G. Mel'nik, L. N. Dubrovskiy. Method of protection of silicon crystals. Avt. svid., No. 137893, Byul. izobr., No. 9, 1961.
10. A. A. Panov. Method of forming of aluminum foil for electrolytic capacitors. Avt. svid., No. 121324, Byull. izobr., No. 14, 1959.
11. A. Riz. Chemistry of crystals with defects. Foreign Literature Press, M. --L., 1956.
12. B. Vercerk, P. Winkel, D. de Groot, Phil. Res. Rep., 13, 6, 506, 1958.
13. E. Verwey. Z. Kristallogr., 91, 3/4, 317, 1935.
14. N. D. Dankov, D. V. Ignatov, N. A. Shishakov. Electrographic investigation of oxide and hydroxide films on metals. Academy of Sciences of USSR Press, M., 1953.
15. H. Ginsberg, Z. Metallkunde, 48, 6, 357, 1957.
16. R. Audubert, A. Roult, J. chim. phys et phys. -chim., 37, 5, 101, 1940.

17. J. Kronsbeyn. Trans. Electrochem. Soc., 94, 353, 1948.
18. N. Mott and R. Gurney. Electronic processes in ionic crystals. Foreign Literature Press, M., 1950.
19. N. Mott. Trans. Farad. Soc., 43, 429, 1947.
20. E. A. Gulbransen, I. Wysong. J. Phys. Chem., 51, 429, 1947.
21. N. Cabrerra and N. Mott. Rept. Progr. Phys., 12, 163, 1948-1949.
22. A. Charlesby. Proc. Phys. Soc. Lond., B 66, 317, 1953.
23. J. Herenguell, P. Lelong, C. r. Acad. Sci., 252, 2218, 1951.
24. S. J. Basinca, J. J. Polling, A. Charlesby, Acta Metallurgica, 2, 312, 1954.
25. D. A. Vermilyea, Acta Metallurgica, 1, 282, 1953.
26. L. Young, Trans. Farad. Soc., 50, 159, 1954.
27. A. R. Bray, P. W. Jacobs, L. Young, Proc. Phys. Soc., 71, 3, 405, 1958.
28. J. F. Dewald, J. Electrochem. Soc., 102, 1, 1955.
29. C. P. Bean, J. C. Fischer, D. A. Vermilyea, Phys. Rev., 52, 4, 515, 1956.
30. L. N. Zakgeym. Electrolytic capacitors. State Power Engineering Publishing House, M. --L., 1952.
31. L. Young, Trans, Farad. Soc., 101, 2, 551, 1956.
32. W. Ch. van Geel, C. A. Pistorius, Phil. Res. Rep., 14, 2, 123, 1959.
33. H. E. Haring, J. Electrochem. Soc., 99, 1, 30, 1952.
34. D. A. Vermilyea, J. Elestrochem. Soc., 104, 3, 140, 1957.
35. N. D. Tomashov, DAN USSR, 88, 6, 1023, 1953.

36. V. V. Skorcheletti. Theoretical electrochemistry. State Chemistry Press, M. --L., 1959.
37. G. V. Akimov and Ye. N. Paleolog, DAN USSR, 51, 4, 291, 1946.
38. L. L. Odynets, Tr. II All-Union, conf. on physics of dielectrics, Academy of Sciences of USSR Press, M., 1960.